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16. ABSTRACT

EPA has been involved for several years in developing and demonstrating methods for the control, recycle, and destruction of water pollutants generated in the electroplating and related industries. This paper examines a number of the newer technologies, describes applications in which EPA's R&D program has been involved and presents cost figures generated as the result of these studies. All EPA projects are referenced so that the reader can pursue those of particular interest in greater detail.

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What's being done to help you select the best treatment methods for your operation?

Many techniques are being developed to eliminate or minimize discharges of the primary pollutants of the electroplating industry. Over the years, the Environmental Protection Agency's Office of Research & Development has participated in the study of a wide variety of these techniques, ranging from chemical destruction to physical-chemical concentration and recovery. This paper summarizes the newer routes which are being considered and presents technical and economic results, primarily those derived from EPA-co-sponsored research projects.

By Herbert S. Skovronek & Mary K. Stinson

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In 1972 EPA undertook to establish guidelines for the electroplating industry. These guidelines were intended ultimately to reduce or eliminate all deleterious discharges in response to PL 92-500. The culmination of the survey of the industry was a set of guidelines[1] for Best Practicable Technology Currently Available (BPTCA) based on square footage plated. The resulting "BPTCA" guidelines were as shown below for cyanide and the four metals of primary concern: chromium, zinc, nickel and copper.

The limitations established at that time for Best Available Treatment Economically Achievable (BATEA) by 1983 called for "zero" pollutant discharge. However, at this time BPTCA has been temporarily "suspended" and BATEA has been "revoked" pending further analysis.

For new plants, those which began construction after 1977 but before 1983, it was determined that discharges would be allowed, but basically at one-half that allowed for BPTCA. Complete pretreatment guidelines, the treatment requirements for plants discharging to municipal treatment facilities, have not yet been promulgated. Interim final regulations for the electroplating industry, limiting the concentration of CN,A (cyanide amenable to chlorination), CN,T (cyanide, total), Cr,VI (hexavalent chromium) and establishing the allowable pH within the range of 7.5 to 10.0 have, however, been issued.[2] Limitations on metals should be released soon.

The emphasis in this paper will be on reviewing several of the newer wastewater treatment technologies, particularly those for rinsewaters, in order to alert the electroplating industry to possible options which may be suitable and necessary alternatives for specific problems. In each case, it is assumed that maximum efforts to reduce pollutants from improper housekeeping, overflows, accidental discharges, etc. have been incorporated in the plant operations—along with an educational program which makes the operators aware of the problems and the goals of the treatment.

In carrying out developmental and/or demonstration projects such as those which will be noted in this paper and summarized in Table I, several points must be taken into consideration: first, **all technologies cannot be evaluated.** EPA staff familiar with the industry must make a judgment as to what appears to have potential for the metal finishing industry while simultaneously trying to perceive how and where such a technology may be applied in other industries. Secondly, **no one project, no one technology can be considered as a panacea for an entire industry.** Each process may offer an opportunity to reduce one or two major problems in an industry. Further, **the results obtained in a specific evaluation of an individual technique at a single plant are not necessarily transferable to nor applicable to other plants, even those appearing on first examination to have the same basic problem.**

Therefore, the success or failure of a technology at a single facility must be examined with great care by the members of the industry. Variations in minor bath additives, processing sequences, general handling, etc. can all have a profound effect on certain waste treatment processes—as they certainly have on the industry's primary operations. EPA sponsored projects are intended as "catalysts" from which firms in the industry can develop customized processes uniquely applicable to their own situations by carefully comparing the demonstration work with their own operations, both from a technical and from an economic point of view.

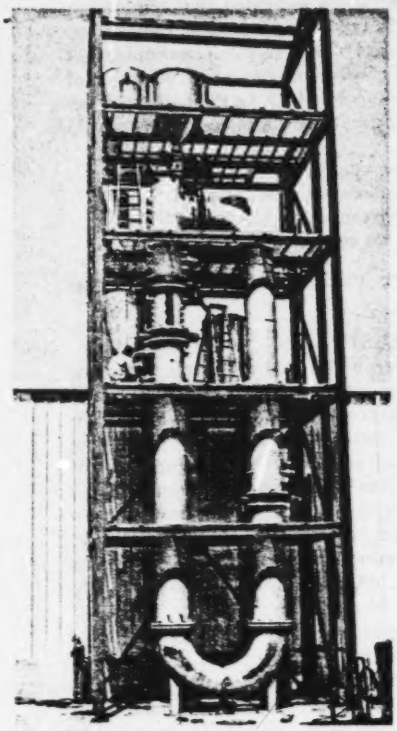
At the current time, the industry has available to it several technologies to meet BPTCA requirements. These technologies have, basically, been in use for several years. For cyanide removal treatment with alkaline chlorine (or hypochlorite) remains the standard technology with higher Cl_2/CN ratios, extended treatment and elevated temperature used to destroy complexed cyanides. For reduction of hexavalent chromium, several techniques are in use, but sulfur dioxide remains the prominent one. For removal of dissolved metals from either alkaline plating or reduced chromium wastewaters, pH adjustment to form carbonates or hydroxides which can then be removed as sludges remains the standard route. These techniques can be integrated into the rinsing cycles to give the

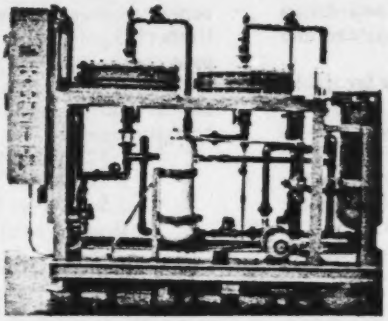
BEST PRACTICABLE TECHNOLOGY CURRENTLY AVAILABLE

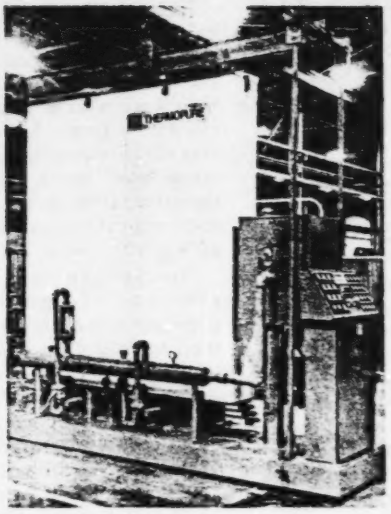
	1 day max.	*30 day avg. max.*
CN (total)	160 mg/m²	80 mg/m²
Cr (VI)	16	8
Cr (total)	160	80
Ni	160	80
Cu	160	80
Zn	160	80

TABLE I — STATUS OF EPA PROJECTS

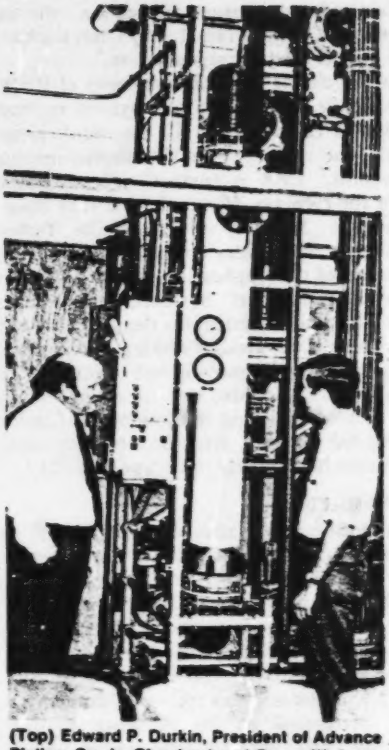
EPA Project No.	*Recipient*	*Technology*	*Status*
12010 DMF	Beaton & Corbin	Integrated Treatment	Complete; available as EPA-R2-73-044
802637	Douglas & Lomason	Ion exchange	Complete; available as EPA-670/2-75-015
802637	Douglas & Lomason	Ion exchange	Ongoing
804434	Houdaille Industries, Inc.	Ion exchange and Integrated Treatment	Ongoing
803781	Advance Plating	Evaporation	Report in preparation
803261	Alcoa	Evaporation	Report in preparation
802254	Anaconda	Cementation	Complete; available as EPA-670/2-74-008
803226	Anaconda	Cementation	Complete; available as EPA-670-2-75-029
12010 GUG	New England Plating	Electrolytic	Complete; available as EPA-600/2-75-028
803342	Atomics International	Electrolytic	Complete; available as EPA-600/2-76-296
12010 DOT	University of Waterloo	Electrolytic	Complete; available as EPA-670/2-74-059
803265	Metal Plating Corporation	Kastone® Process	Complete; available as EPA-600/2-77-038
802924	Metal Finishers' Foundation	Sulfide Precipitation	Complete; available as EPA-600/2-77-049
804648	Holley Carburetor	Sulfide Precipitation	Ongoing
IAG D7-01176	Tobyhanna Army Depot	Sulfide Precipitation	Ongoing
802335	Sealectro Corporation	Ozone	Complete; available as EPA-600/2-77-104
804710	New Jersey Institute of Technology	Electrodialysis & Ion Flotation	Ongoing
804438	Vanderbilt University	Floc Foam Flotation	Ongoing
804710	New Jersey Institute of Technology	Electrodialysis & Ion Flotation	Ongoing
WPRD201-01-68	Metal Finishers' Foundation	Activated Carbon & other techniques	Complete, available as EPA 12010 EIE 11/71
WPRD201-10-68	Metal Finishers' Foundation	Activated Carbon & other techniques	Complete, available as EPA 12010 EIE 03/71
802113	Metal Finishers' Foundation	Activated Carbon	Complete; available as EPA-670/2-75-055
804656	University of Delaware	Activated Carbon	Ongoing
IAG D5-0714	Department of Agriculture	Starch Xanthate	Report in preparation
12010 DRH	The State of Minnesota Pollution Control Agency	Reverse Osmosis (Survey)	Complete; available as EPA 12010 DRH 11/71
803264	American Electroplaters' Society	Reverse Osmosis (NS-100 membrane)	Complete; available as EPA-600/2-76-187
800945-01	American Electroplaters' Society	Reverse Osmosis (Survey)	Complete; available as EPA-600/2-77-261
800945-02	American Electroplaters' Society	Reverse Osmosis (Copper cyanide field test)	Report in printing
803753-01	American Electroplaters' Society	Reverse Osmosis (Watts nickel field test)	Complete; available as EPA-600/2-77-039
803753-02	American Electroplaters' Society	Reverse Osmosis (Zinc cyanide field test)	Ongoing
803620	American Electroplaters' Society	Reverse Osmosis (PBI membrane)	Report in preparation
804311	American Electroplaters' Society	Reverse Osmosis (new membranes, pilot plant)	Ongoing
805300	American Electroplaters' Society	Reverse Osmosis (full-scale mobile unit)	Ongoing
12010 DFS	RAI Research Corporation	Electrodialysis	Complete; available as EPA-R2-73-287
803742	Risdon Manufacturing	Electrodialysis	Report in preparation
803304	Keystone Lamp Manufacturing	Electrodialysis	Report in printing
804655	Seaboard Metal Finishing	Donnan Dialysis	Ongoing
804682	American Electroplaters' Society	Coupled Transport Membranes	Report in preparation
803723	Bumper Recycling Association	ZDS™ system	Report in preparation
803332	Texas Southern University	Solvent Extraction	Report in preparation
12010 FXD	Metal Finishers' Foundation	Sludge Treatment	Complete; available as EPA-670/2-75-018
803787	Metal Finishers' Foundation	Sludge Treatment	Report in printing







(Top) The unique loop ion exchanger full-scale prototype phosphoric acid recovery unit currently being demonstrated at the Douglas & Lomason plant in Cleveland, MS. (Top right) Eco-Tec's nickel salt recovery unit; two of these units are in use at Houdaille's Huntington, WV installation.



(Top) Edward P. Durkin, President of Advance Plating Co. in Cleveland and Roger W. Lacy, Project Engineer with Corning Glass Works, discuss the evaporative system for recovering chromic acid from chrome plating rinse water. (Left) Alcoa's evaporative process unit that can utilize waste heat.

Lancy or Integrated Systems improved treatment efficiency and reduced cost.

Both batch and integrated systems do generate a difficult-to-handle sludge which traditionally has been disposed of via ocean disposal or landfilling. Both these options may become less available over the coming years due to heavy metal toxicity, leaching, and other problems.

ION EXCHANGE

Ion exchange is another technique which has been known for several years and which has been implemented to some degree by the industry. Unfortunately, inexperience with such systems requiring regeneration, and the need still to treat and dispose of the regenerant solutions—now containing the plating pollutants in concentrated form—have left many of these installed systems inactive.

Ingenuity in designing ion-exchange systems enabling material recovery and producing effluent suitable for discharge increases the utility and economics of this technique. For example, Lancy's Laboratories of Zelienople, PA invented a unique ion-exchange process to recover phosphoric acid used in the bright finishing of aluminum.[4] The invention is based on a phenomenon called "acid retardation," wherein the acid is preferentially adsorbed on strong base ion-exchange resin from a solution containing both a strong acid and its salt.

EPA demonstrated this approach in a pilot plant study under a grant to the Douglas & Lomason Company, Detroit, MI. A continuous ion-exchange system was employed to separate the aluminum contamination from a spent phosphoric acid waste generated by bright finishing of aluminum parts. The anion resin accomplishes the separation by "retarding" elution of the phosphoric acid as the processing solution flows through the bed. The aluminum remains in the waste solution and passes out of the column in the effluent. The acid is then eluted from the bed with water, eliminating the use of chemicals for the regeneration of resin bed.

A full-scale prototype phosphoric acid recovery unit is being demonstrated at the Douglas & Lomason plant in Cleveland, MS under EPA Grant No. S-802637. The unit is designed to treat 6,624 l/day (1750 gal/day) of 35 per cent feed liquor with at least 75 per cent recovery of the input H_3PO_4. This level of recovery corresponds to savings of $166,000/year in raw purchased acid. Prototype operating data during the early periods of operation were promising. Later the unit suffered a number of mechanical failures and has now been disassembled for repairs and replacement of parts. Both Lancy and Douglas and Lomason plan to correct the difficulties and place the unit back into operation in the near future.

Another attractive ion-exchange system, called Reciprocating Flow Ion Exchange (RFIE), has been perfected by Eco-Tec Limited (a division of Wix Corporation, Ltd. of Toronto, Ontario) for recovery of waste metals from plating operations.[5] The Eco-Tec system uses two reciprocating flow ion exchange beds. One bed contains cation exchange resin and the other bed contains a combination of anion exchange resins. The system is based on the use of a very short column and utilizes rapid cycling to achieve ion exchange with greater efficiency. The short bed also allows the use of fine resins to maximize surface area and again to increase the rate of exchange. In addition, fine resins are less susceptible to fluid flow problems. Regeneration of the resin bed is countercurrent. Incorporation of all these features results in a much smaller piece of equipment when compared with conventional ion-exchange. Of course, there is an effluent stream from the ion exchange regeneration which must be treated, in most cases.

To date about one hundred Eco-Tec units have been installed in North America and Europe for recovery of all types of Watts nickel and for two types of Cr^{+6} wastes: dilute plating rinsewater and concentrated spent bath. Eco-Tec systems are also being

(Continued on page 34)

employed for recovery of sulfuric acid from sulfuric acid anodizing. In the latter application, the acid retardation phenomenon applies (see Lancy's ion exchange system) and water only is used for regeneration.[6]

Eco-Tec claims that the economics of RFIE are favorable. For example, installation of a system recovering 5 kg/hr of nickel salts (22 per cent Ni) can result in savings of up to $38,000/year and a pay-back on capital investment as short as 7.7 months.[5] EPA is currently demonstrating the Eco-Tec system for recovery of nickel from four rinse systems at the Huntington Division of Houdaille Industries, Inc. in Huntington, WV under Grant No. 804434. Effectiveness and economics of this application will be fully documented.

The Life Support Systems, Inc. company has been developing a novel system for the use of ion exchange resins in the treatment of metal finishing rinsewaters. Basically the system consists of a moving bed of ion exchange resin which passes from wastewater and rinse tank to regeneration and back, thereby achieving continuous purification. EPA has not participated in this program to date, but a pilot scale installation has recently been reported.[7]

EVAPORATION

Evaporation is yet another system which has seen interest over the years, particularly with the more expensive metals and with heated plating baths where concentrates could be returned directly to the plating bath. Corning has recently presented the industry with a new vapor recompression-based thin-film evaporator which it is hoped would rekindle interest in this technique for resource recovery. In a recently completed EPA project, chromic acid was recovered using this equipment.[8] The study, performed at the Advance Plating Company in Cleveland, OH showed that under typical plating shop conditions, the consumption of chromic acid could be decreased by 80 per cent. Recovery can reduce the chromic acid in the effluent from dragout by 99.98 per cent. Economic analysis reveals that, for each kilogram of chromic acid recovered, savings of approximately $1.10 over the purchase of new chrome can be achieved. When a chemical treatment of chrome is considered as an alternative, the savings can be even higher. For example, assuming a cost of chemical treatment of $2.20/kg ($1.00/lb) of chrome, then the total savings realized per kg of chrome is $3.30 ($1.50/lb).

Of course, the big concern of the industry in today's energy-conscious era will be the energy requirements for such a system. Use of waste heat can help to make the evaporative process economically attractive. For example, Alcoa has developed an evaporative process that can use waste heat and which operates at low temperatures and near atmospheric pressures. This process has been demonstrated for treatment/recovery of phosphate-containing effluent from aluminum coil-cleaning operations at Alcoa's Warrick County, IN plant.[9] Operation of a 75,700 l/day (20,000 gal/day) pilot plant showed that the product condensate can be used as rinsewater at the phosphate cleaning lines in place of deionized water, and the concentrated phosphate blowdown can be recycled as make-up to the phosphate cleaning solution. Alcoa plans to commercialize this evaporative process for treatment of a variety of industrial effluents.

CEMENTATION

Cementation, i.e., the displacement of a metal from solution by a metal higher in the electromotive series, is a technique long used by the copper ore industry to recover traces of copper from solution by passing it over scrap iron. EPA has now completed a full scale study[10,11] of this technique as a means of removing copper sulfate from plating wastewaters at Anaconda's Ansonia and Waterbury brass mills. In this project, the wastewater was passed over scrap iron and the copper and iron exchanged. The resulting copper could then be recovered as the metal, while the ferrous sulfate was discharged. In the same process, reduction of contaminating hexavalent chromium by scrap iron also takes place, thus eliminating the need for a separate chromium reduction system.

Economic analysis of the study indicated that the annual copper recovery cost was $23,641 for an average flow of 700 l/min (185 gal/min) (8 hr/day) of feed solution containing 188 ppm copper and 3.69 ppm chromium. Assuming the value of the copper in a usable form to be $1.65/kg ($.75/lb), the net annual return using 15-year amortization of equipment would be approximately:

$22,600 at 90 per cent copper recovery
$16,200 at 75 per cent copper recovery
$ 5,200 at 50 per cent copper recovery
Break-even at 35 per cent copper recovery.

During the course of the project, copper recovery was approximately 55 per cent.

ELECTROLYTIC PROCESSES

Electrolytic techniques can be applied to plate out metals, oxidize cyanide or reduce chromium from wastewaters; electricity is the only operating cost and no chemicals are added. Electrolytic destruction of metallic cyanide wastes has long been known as a means of reducing the concentration of cyanide in spent plating baths. Although this technique was very effective at reducing (high) bath cyanide concentrations to much lower levels, the electrical resistance of the solution increases rapidly as the ion concentration decreases. Thus, the conventional electrolytic techniques simply become too costly at $N \leq 100$ ppm of CN^- to be useful.

Over the past several years a number of approaches have evolved to overcome the electrical resistance of the cell. One approach is that a bed of conductive particles, usually carbon, is used to reduce the resistance of the path the electrons must travel.

Several years ago EPA evaluated such a technique (invented by Joe Shockcor), employing semiconductive beds of carbon particles in a full-scale demonstration at New England Plating, Worcester, MA for both the reduction of hexavalent chromium and the oxidation of cyanides in plating rinsewaters.[12] The heavy metals were subsequently removed from the wastewater by alkali precipitation. Separate 75 l/min (20 gal/min) sized cells were employed for chromium (up to 250 ppm Cr^{+6}) and cyanide (up to 150 ppm CN^-) rinses. Data were also obtained in parallel using conventional chemical treatment for cost comparison. The study showed that the operating costs for chromium treatment were as follows:

Feed Solution	*Cr^{+6} at 17 ppm*	*Cr^{+6} at 156 ppm*
Electrochemical reduction followed by chemical precipitation	$17.20/kg Cr ($7.82/lb)	$2.94/kg Cr ($1.34/lb)
Chemical reduction and precipitation	$15.50/kg Cr ($7.04/lb)	$4.50/kg Cr ($2.04/lb)

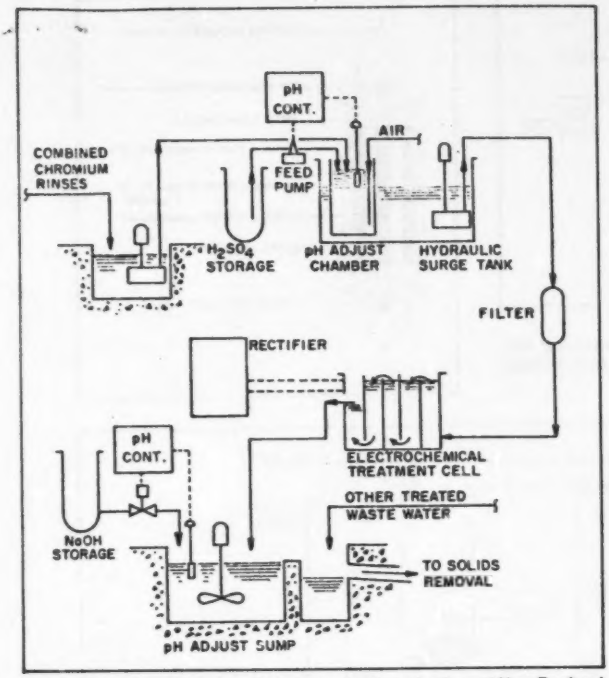
It is apparent that electrolytic reduction is economical for higher chromium concentration. However, the electrolytic chromium reduction equipment cost was three times higher than that for a comparable chemical system.

Operating costs for cyanide oxidation were as follows:

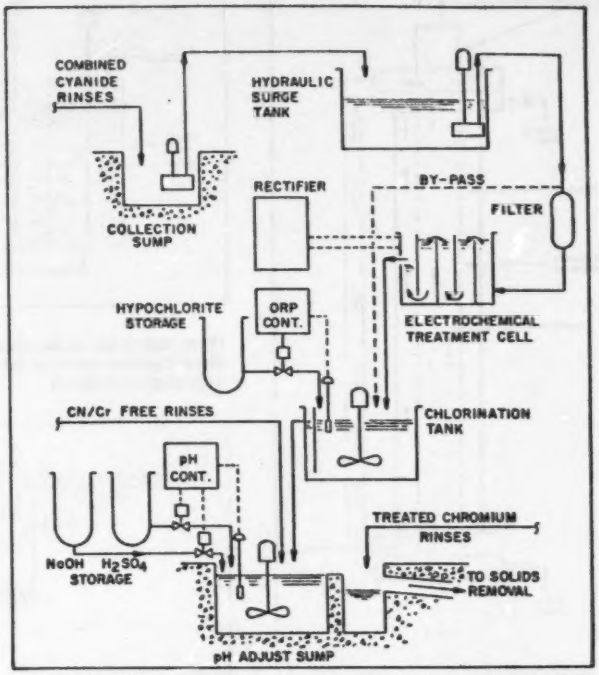
Feed Solution	*CN^- at 102 ppm*
Electrochemical/chemical oxidation to $Co_2 + N_2$ (at 65 per cent by electrolysis, 35 per cent by chlorination)	$4.14/kg CN^- ($1.88/lb)
One-step chemical oxidation to cyanate	$5.14/kg CN^- ($2.34/lb)

In cyanide oxidation, the electrochemical process reduced direct costs associated with subsequent chlorination. Note that a two-step chemical oxidation of CN^- to $Co_2 + N_2$ would be $11,000 per year more costly than the electrolytic method.

More recently, Atomics International has developed a



Schematic of the chromium rinse water treatment set-up at New England Plating, Worcester, MA.



Schematic of the cyanide rinse water treatment set-up at New England Plating, Worcester, MA.

particle bed system that concurrently removes metals and oxidizes cyanide. The system employs an electrolytic cell with a cathode bed composed of tin particles, a graphite particle-bed anode and a cellophane separator. Low voltage DC is applied. Best removals were obtained with NaCl added as a supporting electrolyte and with recirculation of the anode bed effluent. A small, 1.9 l/min (0.5 gpm), pilot-plant unit was demonstrated under EPA Grant No. R-803342 to the Metal Finishing Foundation on cadmium and zinc rinsewaters at a plating plant.[13] Two-stage operation gave overall removals of 95 per cent of an initial 22 ppm cadmium and 94 per cent of an initial 44 ppm cyanide. Similar two-stage treatment of zinc rinsewaters gave overall removal of 75 per cent of an initial 57 ppm zinc and 78 per cent of an initial 195 ppm cyanide. Treated wastewater could be reused as rinsewater.

Based on the actual test results at the plating plant, an estimate of process economics was made. The estimated total treatment costs are \$17.65/1000 m^2 (\$1.64/1000 ft^2) plated, with cadmium plating rinsewater use at 13 l/min (3.5 gpm) for 230 m^2 hr (2,500 ft^2/hr) and 40 hr/week operation. However, the economics of a commercial system may differ from the values derived from the pilot plant system.

In another approach, the mean path between the electrodes is reduced by simply using a narrow tube through which the rinsewater must pass. In the design developed by Waterloo University under EPA Grant No. 12010 DOT[14] concentric tubes are used as the anode and cathode. Cyanide reductions from about 100 ppm to an effluent level of 0.5 ppm were achievable. Although this work was only on the laboratory scale, cost estimate for a full scale system capable of treating 820 kg (1800 lb) CN^- load per year (at a 100 ppm influent CN^- level to achieve less than 1 ppm CN^- in the effluent) was about half the cost of comparable chemical treatment. Increases in electricity costs in recent years could make such electrolytic techniques less economical in comparison with chemical treatment, however.

Novel electrolytic cells, structured to provide a high surface area, are emerging in Europe and the U. S. for treatment recovery of dilute metal-containing effluents. Ecological Engineering's Eco-Cell (Great Britain)[15] features a concentric cathode and anode, separated by an ion-exchange membrane and a cavity through which the wastewater passes. The cathode rotates inside the cell, while the anode remains stationary. The system is effective for metal loads from 100 to 100,000 ppm and the effluent concentration achievable is in the range of 2-10 ppm. The metal is concentrated as a powder/water mixture and can be recovered. The system is close to commercialization and the capital cost of the Eco-Cell system is reported to be \$15,000 for 12,800 l hr (3,200 gal hr) of effluent containing 368 ppm copper.

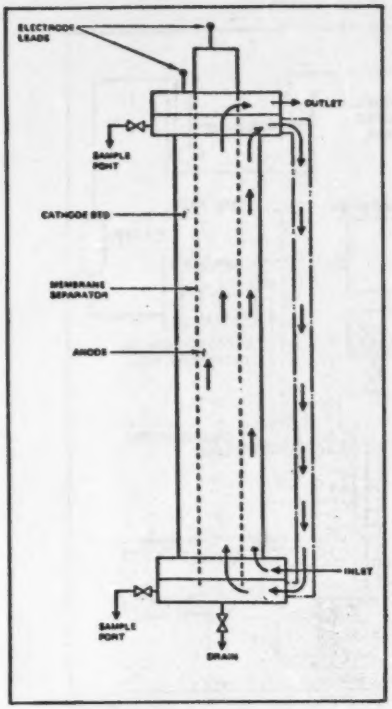
DuPont's Extended Surface Electrolysis (ESE) system[16] aims at more dilute wastestreams containing 100 ppm or less of metal. The ESE spiral cell is a sandwich construction containing a fixed, "fluffy" (stainless steel mesh) cathode, a porous separator layer, a screen-like material as the anode, and another separator layer. This sandwich is rolled up into a spiral "jelly roll" and inserted into a pipe. The compact cells have an open structure, with a very high void volume that provides a low resistance to fluid flow. The ESE cell has been successfully tested on a pilot plant scale, mainly on a copper stream, but should also be suitable for recovery of other heavy metals. Typical efficiencies reported are on the order of 90 per cent. Preliminary economics favor ESE versus ion exchange for dilute streams. DuPont plans to commercialize the system in the near future.

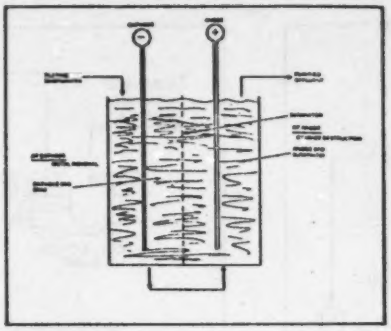
ADVANCED CHEMICAL TECHNIQUES

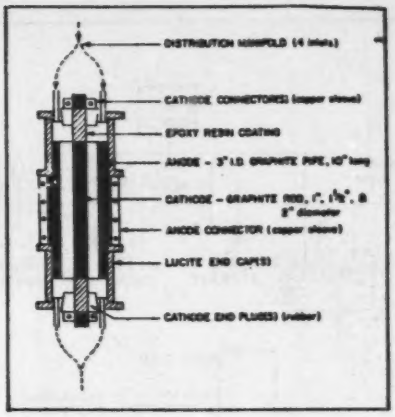
One of the more conventional techniques is DuPont's Kastone process, which uses hydrogen peroxide and formalin at elevated temperature to oxidatively destroy cyanide. An added advantage, it is claimed, is that the process converts the metal ions to insoluble oxides rather than hydroxides, and that these oxides settle more readily and more completely, giving a dense sludge and thus, lower residual suspended solids levels.

It should be noted, however, that the BOD_5 of the effluent is increased by the formation of an organic acid, glycolic acid. Under certain conditions this could be undesirable.

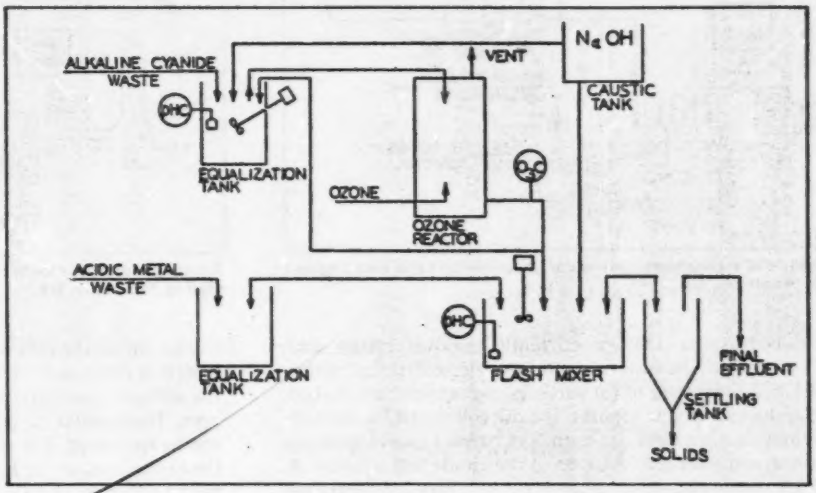
The Kastone process can be made more attractive if the resulting zinc oxide sludge is redissolved and returned to the plating process. EPA has recently demonstrated, in Grant No. S-803265,[17] the feasibility of zinc metal recovery from Kastone sludge. The study, carried out at the Metal Plating Corporation, Connersville, IN showed that an adequate system to redissolve zinc oxide sludge can be designed and operated.






DISTRIBUTION MANIFOLD (4 inlets)
CATHODE CONNECTOR(S) (copper sleeve)
EPOXY RESIN COATING
ANODE – 3" I.D. GRAPHITE PIPE, 10" long
CATHODE – GRAPHITE ROD, 1", 1 1/8", & 2" diameter
ANODE CONNECTOR (copper sleeve)
LUCITE END CAP(S)
CATHODE END PLUG(S) (rubber)

(Top) Schematic of Atomics International PBE Metal-Cyanide Removal Unit. (Left) Schematic of pilot-plant unit cell.



(Right) Flow diagram of the Sealectro Plating waste treatment plant. (Top right) Annular flow reactor for electrolyzing aqueous CN^- solution.

Savings will result from lowered anode usage in the plating process as well as from the recovered zinc value. Economics derived from this study show that it takes $4.53/day investment to treat the cyanide stream and $5.53/day investment to treat and recycle the sludge. Where transportation costs to landfill are high, the recycling of sludge would provide an additional economic incentive.

Recognizing that future restrictions on heavy metals would require much more complete removal of these materials, more than achievable by pH adjustment and precipitation, the Permutit Company has developed a process called "Sulfex." In this process, the first hydroxide precipitation would be followed by a treatment with sulfide ion to convert residual dissolved metal ions to much more insoluble metal sulfides. Although one might think that the hydroxide precipitation step could be replaced totally by the sulfide procedure, practical constraints such as the low solubility of any usable sulfide ion source precludes such an approach.

The Sulfex process employs a sparingly soluble and non-toxic ferrous sulfide (FeS) as a source of sulfide ion. The principal reactions are as follows:

$$Cu\ EDTA^{-2} + FeS_{(s)} = CuS_{(s)} + Fe\ EDTA^{-2} \quad (1)$$

$$FeS_{(s)} + 2H_2O = Fe^{++} + 2OH^- + H_2S(g) \quad (2)$$

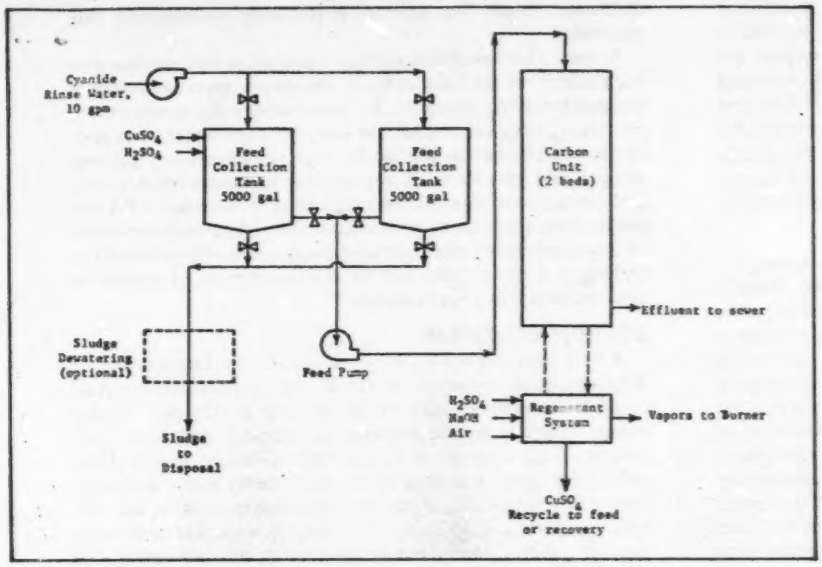
The first reaction shows that FeS is effective in breaking up complexes and precipitating heavy metal sulfides. The second reaction shows that the FeS - H_2O system is self-regulating with respect to the sulfide content of the solution. The amount of H_2S vapor in the air above a saturated FeS solution remains constant, regardless of the amount of FeS added. This constant amount of generated H_2S by the FeS-H_2O system is only 0.003 ppm, which is below the odor detectable level. Thus, the use of FeS in the Sulfex process offers a significant advantage over the use of soluble sulfide sources (NaHS or Na_2S) which generate hydrogen sulfide by hydrolysis of the excess reagent and require strict control of both pH and reagent addition to avoid odor and safety problems and would be disastrous to any bright metal surface in the vicinity.

In a recently completed joint EPA-Metal Finishing Foundation project at the Permutit Research and Development Center, Princeton, NJ,[18] the Sulfex process was compared to conventional hydroxide precipitation in laboratory and pilot plant studies. The study demonstrated that Sulfex is technically feasible and superior to conventional hydroxide precipitation for removal of copper, cadmium, nickel and zinc. Hexavalent chromium also can be removed by Sulfex in a one-step operation within the pH range of 8 to 9.

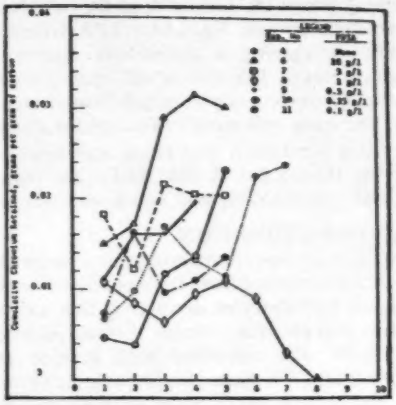
The effluent quality depends on the type of complexing agents present, but the process is effective for metals complexed with EDTA and Rochelle salt. Without complexing agents, the achieved effluent quality for all metals is on the order of ≤ 0.05 ppm. The process is generally more effective for a solution of mixed metals rather than a single metal.

Preliminary economics indicate that Sulfex should be practical as a polishing treatment following hydroxide precipitation or when the effluent contains up to 50 mg/l of dissolved heavy metals. To evaluate operating parameters and to determine the real economics, the system is presently being demonstrated on-stream under EPA Grant No. 804648 at Holley Carburetor, Paris, TN. However, questions of total treatment cost, including disposal of mixed hydroxide and sulfide sludges, still remain unresolved.

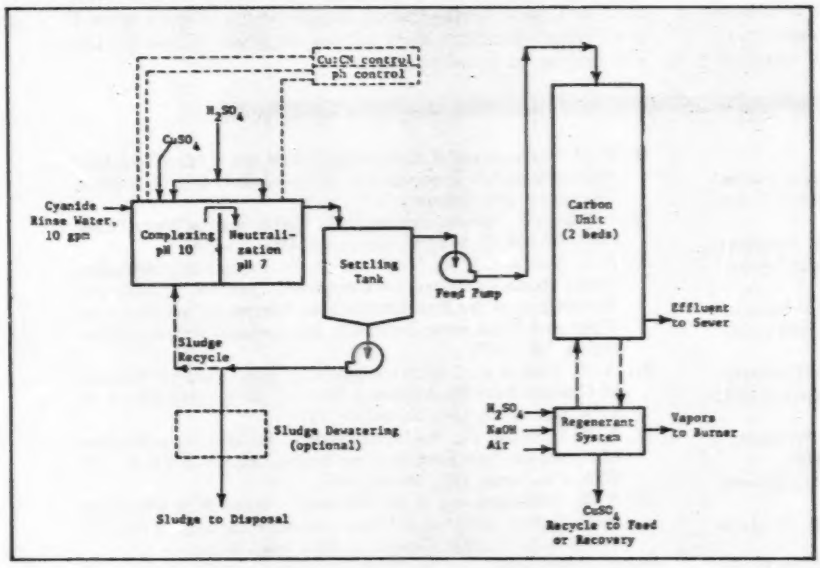
Another project underway at the Tobyhanna Army Depot, PA (IAG-D7-01176) is further evaluating other aspects of sulfide precipitation.

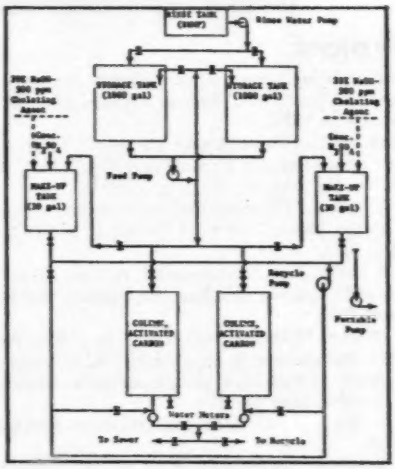


(Top, from Battelle Columbus) System I: Flow diagram of batch or manually operated carbon process. (Below) System II: Flow diagram of continuous carbon process.



(Top) Chromium retained on carbon after adsorption-desorption cycles. (Below) Schematic diagram of activated carbon adsorption unit.





Ozone is gradually being recognized as one of the most valuable oxidants, both for industrial and for municipal wastes. Several years ago its use for destruction of a waste containing cyanide and phenols had been initiated by Boeing in Wichita, KS. This installation is still in operation. EPA has now cooperated in a project at Sealectro Corp. where destruction of cyanide-bearing electroplating wastes to a residual of < 1 ppm CN^- has been successfully demonstrated.[19] Although sludge volume at this small parts plating shop was too small to study in detail, observations indicated that it settled readily and/or was filterable, much more so than the traditional hydroxide sludge. The total cost of CN^- treatment (operating plus capital) at this small plant was calculated as \$0.62/1000 l (\$2.35/1000 gal) for a wastewater containing 20 ppm CN^-. Copper appears to catalyze the CN^- destruction, confirming earlier studies.

Although ozone is very effective for free cyanides, it is well known that certain cyanide-metal complexes, particularly that of iron and nickel, are more stable and resistant to both ozone destruction and conventional alkaline chlorine treatment. Some years ago it was discovered that exposure of rinsewater containing such complex cyanides to low intensity ultraviolet light irradiation during ozonation would facilitate cleavage of the complex and oxidation of the cyanide. For very stable complexes it was found that elevated temperature was also necessary.[20]

A pilot plant has recently been built by Houston Research and shipped to France to evaluate this technique on a wastewater containing complexed cyanide. This concept (UV + ozone) is being recognized as a broadly useful technique for destruction of a wide variety of stable organic pollutants, but has not yet been given a full scale test on cyanide wastes. Its applicability to this industry and cost are, therefore, unknown at this time.

TREATMENT OF FLUOBORATES

Replacement of cyanide ions with other bath constituents may also minimize environmental problems. For example, the use of the fluoborate ion to replace the cyanide and sulfate ions in a plating bath is becoming increasingly popular with major plants. The fluoborate ion is much less toxic than the cyanide ion and thus provides a safer working environment. Fluoborate plating offers the plater many advantages such as a high quality product ("jewelry quality") and easy process control.

Among disadvantages are high cost of the reagent and the lack of practical treatment or recovery processes for fluoborate

containing rinses. Dr. Liskowitz of the New Jersey Institute of Technology, Newark, NJ, under EPA Grant No. 804710, is presently developing a closed-loop treatment system for fluoborate rinses. The system will employ electrodialysis and ion flotation to recover and recycle fluoborate, surfactant and water. The study will result in a design for a pilot-scale system. (Floc foam flotation is also being investigated at Vanderbilt University (Grant No. R-804438) for the removal of metals from both electroplating and non-ferrous metal wastewaters.)

CARBON ADSORPTION

Several years ago, in carrying out a preliminary survey for EPA of treatment methods for metal finishing wastes, Battelle Columbus Laboratories discovered that carbon adsorption, normally thought of as a means of removing organic pollutants from water, also adsorbed both cyanide and hexavalent chromium ions.[21,22] Regeneration was, however, only partially successful in each case. Further work has now been carried out on the more promising of these techniques, the removal of hexavalent chromium, and the regeneration techniques have been improved somewhat. Although hexavalent chromium removals of 99.99 per cent, down from 600 ppm to ≤ 0.05 ppm, can be achieved, regeneration (with caustic) has not yet been brought to the stage where the system can be considered practical.[23]

Very recently, Dr. Huang of the University of Delaware has suggested still further modifications to the regeneration scheme which may improve the overall practicality and economics of the scheme. An EPA co-funded study with the University of Delaware, Grant No. 804656, is presently investigating this possibility.

A somewhat modified carbon adsorption system has also been offered by the Calgon Corp. and does appear to overcome the problem of regeneration. By introducing a slip or sidestream containing divalent copper ion into the wastewater (if copper ion is not present in the waste) and simultaneously passing oxygen into the column, it appears that an in-situ regeneration and oxidation of cyanide ion takes place.[24] Although EPA has not had the opportunity to evaluate this method for destruction of cyanide-bearing electroplating wastes, a modification of the technique is being examined for the destruction of cyanide in petroleum refinery wastewaters.[25]

STARCH XANTHATE

A few years ago Dr. Wing of the U. S. Department of Agriculture laboratory in Peoria, IL reported that heavy metals could be complexed with polymeric poly-xanthates such as a starch xanthate in the presence of cationic polymers. This complex salt formation could remove heavy metals from solution to quite low concentrations, usually below discharge limits. Several modifications and improvements of the scheme, which requires destruction of the complex with acid or heat for recovery of the metals, have now evolved into a process with commercial potential.[26] A co-funded Department of Agriculture, EPA study (IAG D5-0714) at Peoria, IL is now being completed to assess the potential applicability of this process.[27] (Dr. Wing's paper on work conducted under EPA-IAG D5-0714 begins on the next page.)

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This concludes Part I of "Advanced Treatment Approaches for Metal Finishing Wastewaters." Part II, which will address reverse osmosis, electrodialysis, newer membrane techniques, solvent-based systems, freezing, and control options for sludge, will be presented in the November issue.

Full reprints of this paper will be made available at a later date.